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Article

$\eta^1:\eta^2$ -*P*-Pyrazolylphosphaalkene Complexes of Ruthenium(0)

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Abstract: An extended range of novel ruthenium phosphaaalkene complexes of the type $[\text{Ru}\{\eta^1\text{-}N\text{-}\eta^2\text{-}P\text{-}C\text{-}P(\text{pz}')=\text{CH}(\text{SiMe}_2\text{R})\}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Tol}$, $\text{C}_6\text{H}_4\text{CF}_3\text{-}p$; $\text{pz}' = \text{pz}^{\text{Me}_2}$, pz^{CF_3} , $\text{pz}^{\text{Me,CF}_3}$; $\text{R} = \text{Me}$, $\text{C}_6\text{H}_4\text{CF}_3\text{-}p$; $\text{pz}' = \text{pz}^{\text{Ph}}$) have been prepared from the respective ruthenaphosphaalkenyls $[\text{Ru}\{\text{P}=\text{CH}(\text{SiMe}_2\text{R})\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ upon treatment with Lipz' . Where $\text{R} = \text{C}_6\text{H}_4\text{CF}_3\text{-}p$ and $\text{pz}' = \text{pz}^{\text{Me}_2}$ the complex is characterized by single crystal X-ray diffraction, only the second example of such species being structurally characterized. This indicates enhanced pyramidalisation of the alkenic carbon center when compared with precedent data ($\text{R} = \text{Me}$, $\text{pz}' = \text{pz}$) implying an enhanced $\text{Ru} \rightarrow \pi^*_{\text{PC}}$ contribution, which can be correlated with the greater donor power of pz^{Me_2} . This is similarly reflected in spectroscopic data that reveal significant influence of the pyrazolyl substituents upon the phosphaaalkene, stronger donors imparting significantly enhanced shielding to phosphorus; in contrast, a much lesser influence if noted for the silyl substituents.

Keywords: phosphorus; phosphaaalkene; phosphaaalkenyl; pi-complex; pyrazolate

1. Introduction

After almost half a century of study, the chemistry of low-coordinate phosphorus continues to fascinate both organic and inorganic chemists alike [1–8]. Dominated by the isolobal and isoelectronic relationship between phosphorus and the “CH” fragment, the chemistry of phosphacarbons is often familiar from their carbo-centric and nitrogenous counterparts, yet they simultaneously embody appreciable dichotomy in terms of their underlying electronic and chemical nature. Nowhere is this more apparent than in the chemistry of phosphaaalkenes ($\text{RP}=\text{CR}'\text{R}''$) and phosphaaalkynes ($\text{RC}\equiv\text{P}$), which rank among the most heavily studied classes of phosphacarbon. Reactivity is in each case dominated by the high-energy π -systems, though in the case of phosphaaalkenes this is often competitive with the lone-pair, which lies close—albeit marginally lower—in energy. In contrast, the phosphaaalkyne lone-pair is appreciably stabilized, but can be engaged chemically under appropriately directing conditions.

The study of these compounds is, however, often complicated by an intrinsic lack of stability, which restricts the range of available substrates and necessitates some synthetic ingenuity. Such difficulties are often addressed by the imposition of steric bulk, as a means of imparting kinetic stability, which has proven particularly effective in precluding homo-oligomerisation of phosphaaalkenes. The same approach has typically been cited in the development of kinetically stabilized phosphaaalkynes (e.g., $^t\text{BuC}\equiv\text{P}$, $\text{AdC}\equiv\text{P}$), however, in these cases the bulk is often sufficiently remote from the reactive π -system as to preclude it being the sole stabilizing influence. Moreover, even bulky phosphaaalkynes, e.g., $\text{R}_3\text{SiC}\equiv\text{P}$ ($\text{R} = \text{Ph}$ [9], Me [10,11]) often exhibit only limited stability, in some instances comparable to that of unencumbered systems (e.g., $\text{MeC}\equiv\text{P}$ [12]). Significantly, the formally related phosphaaethynylate ion “ $\text{O}-\text{C}\equiv\text{P}^-$ ” is isolable as a sodium salt [13,14], which exhibits appreciable stability despite the lack of any steric “protection”; this fact is attributed to electronic influences, with

the preferential adoption of an $\text{O}=\text{C}\equiv\text{P}^-$ type structure. Taken alongside computational studies of the isolated cyaphide ion ($[\text{C}\equiv\text{P}]^-$), which indicate an intrinsically unstable hypovalent $[\text{C}=\text{P}]^-$ structure [15], this would imply that electronics serve an equally important role in imparting stability to low-coordinate phosphacarbons. Indeed, in the context of phosphaaalkenes—which remain the longest and most heavily studied of the phosphacarbons—the incorporation of π -donor substituents (e.g., NR_2 , OR) and/or conjugate π -systems has long been employed as an alternative means of stabilization [16].

In seeking to further stabilize, and chemically exploit phosphaaalkenes, the incorporation of transition metal fragments has proven to be a particularly valuable tool. Prominently, the coordination of phosphaaalkenes [17] in an η^1 -fashion allows for selective reactivity of the π -system to be developed, by sequestering the lone-pair and precluding its competitive reaction [18]. Somewhat less extensively studied, η^2 -coordination—common among carbo-centric analogues—has also been employed with phosphaaalkenes [19,20], discrimination between η^1 and η^2 being achieved through judicious selection of the metal fragment, though bridging- $\eta^1:\eta^2$ complexes have also been described [21]. Moreover, both transition metal and, to a lesser extent, main-group fragments can be incorporated as discrete substituents on the phosphaaalkenic core to afford a range of metallaphosphaalkenyl complexes (Figure 1) [22,23]. First described in 1985 [24], such systems remain relatively rare, though—with the exception of type E—all possible motifs have been realized, with *P*-metalla- (type A) and *C*-metalla- (type B) systems the most heavily studied.

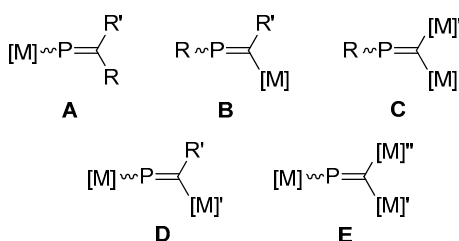
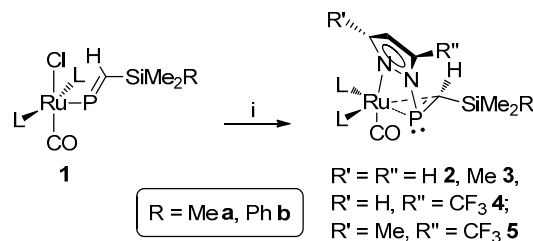


Figure 1. Metallaphosphaalkenyl motifs.

Recently, as part of an extended program investigating transition metal compounds featuring low-coordinate phosphacarbons with potential for conjugation [25–28], we have prepared and studied a range of ruthenaphosphaalkenyl complexes of the type $[\text{Ru}\{\text{P}=\text{CH}(\text{SiMe}_2\text{R})\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$ **1a**, Ph **1b**, Tol **1c**) [29,30]. These are prepared by hydorruthenation of phosphaaalkynes $\text{R}_3\text{SiC}\equiv\text{P}$, following from methodology developed initially by Hill and Jones for $t\text{BuC}\equiv\text{P}$ and related systems [31–33], and superficially related to Nixon’s independent reduction of $[(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-P}\equiv\text{C}^t\text{Bu})]$ with Schwartz’s reagent [34]. Notably, we have described the first structural data for ruthenaphosphaalkenyls, which demonstrate the phosphaaalkenyl moieties to behave as classical 1-electron donors, within a square-based pyramidal metal coordination sphere. Significantly, this precludes, in the ground state at least, any augmenting $\text{P}\rightarrow\text{Ru}$ donation from the lone-pair (i.e., phosphavinylidene character), which is consistent with precedent reactivity studies that demonstrate a nucleophilic phosphorus center [35–39]; indeed, in common with these precedent reports, we have found **1a–b** to engage in reaction with electrophilic fragments at phosphorus [30,40].

Notwithstanding, we have additionally observed an unusual reaction to proceed when **1a** or **1b** is exposed to the lithium pyrazolates $\text{Li}[\text{pz}']$ ($\text{pz}' = \text{pz}$, pz^{Me_2} , pz^{CF_3} , $\text{pz}^{\text{Me,CF}_3}$), giving rise to the unprecedented phosphaaalkene complexes $[\text{Ru}\{\eta^1\text{-N}:\eta^2\text{-P,C-P}(\text{pz}')=\text{CH}(\text{SiMe}_2\text{R})\}(\text{CO})(\text{PPh}_3)_2]$ (Scheme 1) [29,30], which feature an apparent 3-member (Ru-P-C) metallacyclic core, bridged by a pyrazolyl moiety. Also replicated using Hill’s $[\text{Ru}\{\text{P}=\text{CH}(t\text{Bu})\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, this chemistry would perhaps imply ambiphilicity for the ruthenaphosphaalkenyl motif, if not directly of the alkenyl phosphorus center. On the basis of available data, we reasoned the resulting complexes to be best formulated as involving an η^2 -phosphaaalkene moiety, in line with the Dewar–Chatt–Duncanson model, with a dominant contribution from $d_\pi\rightarrow\pi^*(\text{PC})$ retro-donation to metal–ligand binding. The precise extent of the latter might reasonably be influenced by the nature of the phosphaaalkene substituents, or

indeed those of the pyrazolyl moiety, resulting variations in the atom-specific parameters (e.g., NMR shielding effects) offering a potential means of quantification. In seeking to assess the influence of such factors, and thus potentially to elaborate means of control over reactivity, we report herein the synthesis and characterization of an extended range of these novel pyrazolylphosphaalkene complex.

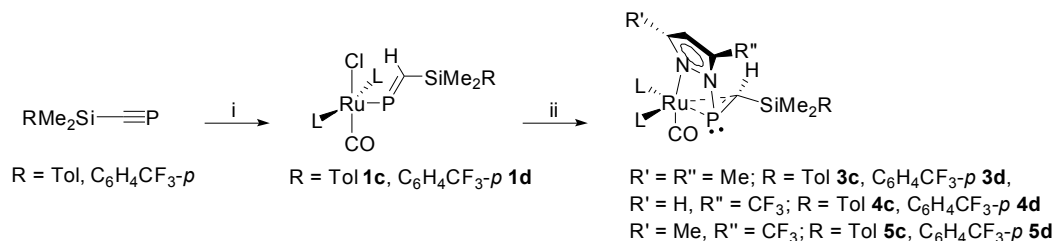


Scheme 1. Synthesis of $[\text{Ru}\{\eta^1\text{-N}:\eta^2\text{-P,C-P(pz')}=\text{CH}(\text{SiMe}_2\text{R})\}(\text{CO})(\text{PPh}_3)_2]$ (**2–5**) [29,30] ($\text{L} = \text{PPh}_3$).
 Reagents and conditions: (i) Lipz' ($\text{pz}' = \text{pz}, \text{pz}^{\text{Me}_2}, \text{pz}^{\text{CF}_3}, \text{pz}^{\text{Me,CF}_3}$), THF.

2. Results and Discussion

2.1. Synthesis and Characterization of η^2 -Pyrazolylphosphaalkene Complexes

As we have previously described [29,40], the ruthenaphosphaalkenyls **1c–d** were prepared via hydorruthenation of the respective phosphalkynes $\text{RMe}_2\text{Si}\equiv\text{P}$ with $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (Scheme 2). Each system is readily identified on the basis of characteristic spectroscopic signatures, *viz.* (i) the heavily deshielded $^{31}\text{P}\{^1\text{H}\}$ -NMR resonance for the phosphaalkenyl moiety; (ii) consistently integrating resonances for two equivalent PPh_3 ligands; (iii) HMBC correlations (^1H – ^{29}Si ; ^1H – ^{31}P) confirming the presence of the silyl group and alkenic proton; (iv) infrared band for the retained carbonyl (ν_{CO} 1930–1950 cm^{-1}), characteristic of a ruthenium(II) carbonyl complex.



Scheme 2. Synthesis of $[\text{Ru}\{\text{P}=\text{CH}(\text{SiMe}_2\text{R})\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Tol } \mathbf{1c}, \text{C}_6\text{H}_4\text{CF}_3\text{-}p \mathbf{1d}$) and their conversion to $[\text{Ru}\{\eta^1\text{-N}:\eta^2\text{-P,C-P(pz')}=\text{CH}(\text{SiMe}_2\text{R})\}(\text{CO})(\text{PPh}_3)_2]$ (**2–5**) ($\text{L} = \text{PPh}_3$). Reagents and conditions: (i) $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, CH_2Cl_2 , 1 h.; (ii) Lipz' ($\text{pz}' = \text{pz}^{\text{Me}_2}, \text{pz}^{\text{CF}_3}, \text{pz}^{\text{Me,CF}_3}$), THF, 1 h.

The reactions of **1c–d** with $\text{Li}[\text{pz}^{\text{Me}_2}]$ each afford a single complex (**3c–d** respectively), which is spectroscopically comparable to those obtained similarly from **1a** and **1b** [29,30]. Thus, the characteristic resonances for the phosphaalkenyl and PPh_3 ligands are lost, being replaced by three new, mutually coupling, resonances (1:1:1 ratio) in the region 50–30 ppm, which is commonly associated with saturated ($\lambda^3\sigma^3$) phosphorus centers. In each case, the lower frequency resonance is identified as that associated with the phosphacarbon, on the basis of a ^1H – ^{31}P -HMBC correlation to the, now appreciably shielded, “ $\text{CH}(\text{SiMe}_2\text{R})$ ” moiety (identified from ^1H – ^{29}Si -HMBC spectra and a significant $^1J_{\text{PC}}$ coupling (~ 70 Hz)). The latter is observed at $\delta_{\text{H}} \sim 1.7$ and $\delta_{\text{C}} \sim 42$, which, though appreciably lower frequency than for a classical alkenyl “CH”, remains somewhat deshielded for a fully saturated “alkyl” moiety. Indeed, as was previously noted for **2a–b** and **3a–b**, the magnitude of the $^1J_{\text{CH}}$ coupling (~ 130 – 140 Hz) is intermediate between those of C_2H_4 (156 Hz) and CH_4 (125 Hz) [41], while $^1J_{\text{PC}}$ are essentially unperturbed from those of the parent phosphaalkenyls, consistent with the case of a π -bound phosphaalkene. This scenario is further supported by a significant reduction in ν_{CO} for

the retained carbonyl ($1900\text{--}1910\text{ cm}^{-1}$), indicative of increased density at metal and, on the basis of calculated force constants, consistent with reduction of the metal to Ru(0) [42–46].

Though augmented by computational data, the direct structural characterization of η^2 -pyrazolylphosphaalkene complexes has been limited previously to the single crystal X-ray structure of pyrazole derivative **2a** and a low-quality structure of **3a** that served to confirm connectivity [30]. However upon prolonged standing at ambient temperature, a concentrated CDCl_3 solution of **3d** yielded X-ray quality single crystals of the chloroform solvate (Figure 2).

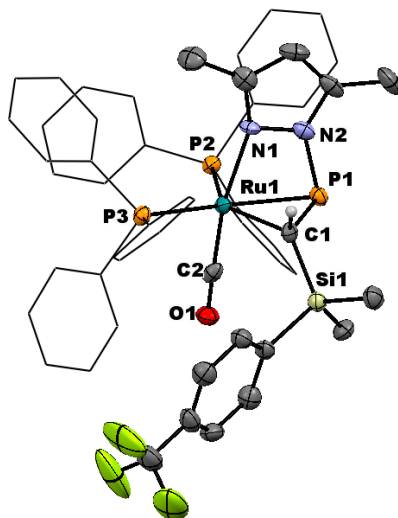
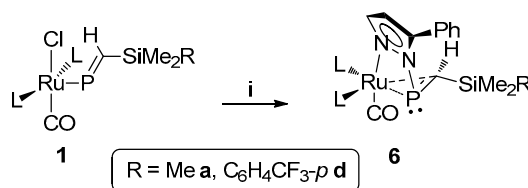


Figure 2. Molecular structure of $[\text{Ru}(\eta^1\text{-N}:\eta^2\text{-P,C-P}(\text{pz}^{\text{Me}_2})=\text{CH}(\text{SiMe}_2\text{C}_6\text{H}_4\text{CF}_3\text{-}p))](\text{CO})(\text{PPh}_3)_2$ (**3d**) in crystals of the chloroform solvate, with thermal ellipsoids at the 50% probability level. Ancillary phenyl rings are reduced, and hydrogen atoms omitted for clarity. Selected bond distance (Å) and angles ($^\circ$): Ru–P1 2.381(1), Ru–P2 2.359(1), Ru–P3 2.369(1), Ru–C1 2.211(4), Ru–C2 1.831(5), Ru–N1 2.229(3), P1–C1 1.782(5), P1–N2 1.778(4), C1–Si 1.860(4), C2–O 1.155(6); Ru–C1–Si 128.2(2), Ru–C1–P1 72.3(2), Ru–P1–C1 62.2(1), Ru–P1–N2 82.5(1), Ru–C1–H1 112.1(4), P1–C1–Si 113.4(2), P1–C1–H1 112.1(4), C1–P1–N2 96.1(2), P1–Ru–P2 93.6(1), P2–Ru–P3 114.0(1), P3–Ru–C1 107.1(1), P1–Ru–C1 43.5(1), P2–Ru–C2 91.1(1), P3–Ru–C2 89.1(2), C2–Ru–N1 170.2(2).

In common with the precedent structure of **2a**, compound **3d** exhibits distorted trigonal-bipyramidal geometry about ruthenium, with PPh_3 ligands and the η^2 -phosphaalkene lying in the equatorial plane. The carbonyl adopts an axial position, along with the metal-pyrazolyl bond, the latter being marginally distorted from linearity ($\angle\text{C}_{\text{CO}}\text{--Ru--N}$ $170.2(2)^\circ$) due to the strain of bridging the Ru–phosphacarbon linkage. Internal angles for the phosphacarbon moiety indicate partial pyramidalization of the carbon center, while the unusually tight angles about phosphorus can be attributed to the constraint of the bridging pyrazolyl group. Taken together with the P–C linkage $1.782(5)$ Å, which is intermediate between a single and double bond [47,48], these data are wholly consistent with our previous conclusion of η^2 -binding, rather than a discrete metallacyclic species. The $\text{C}\equiv\text{O}$ linkage is marginally elongated relative to the structurally characterized ruthenium(II) phosphaalkenyls [30], consistent with a more electron rich metal center, and is comparable to those of other established Ru(0) carbonyls, including that previously reported for **2a**. Indeed, within the bounds of uncertainty, the molecular geometry of **3d** is fully comparable to that of **2a**, with the exception of a marginally contracted P–N linkage ($1.788(4)$ Å, *cf.* $1.809(5)$ Å **2a**), which might reasonably be attributed to the increased donor strength of pz^{Me_2} relative to pz , as is reflected in the spectroscopic features (*vide infra*). Moreover, marginally greater pyramidalization about carbon is apparent in **3d** ($\angle\text{Si--C--P}$ $113.4(2)^\circ$ *cf.* $116.7(3)^\circ$ **2a**), which might similarly reflect the enhanced donor strength of pz^{Me_2} leading to an increase in retro-donation from the metal.

In analogous fashion to the synthesis of **3**, treatment of phosphaalkenyls with $\text{Li}[\text{pz}']$ ($\text{pz}' = \text{pz}^{\text{CF}_3}$, $\text{pz}^{\text{Me,CF}_3}$, pz^{Ph}) led to formation of the respective η^2 -phosphaalkene complexes **4c–d**, **5c–d** (Scheme 2),

6a and **6d** (Scheme 3); the SiMe₃ (**a**) and SiMe₂Ph (**b**) derivatives of **4** and **5** have been previously described [29]. In contrast to **2** and **3**, the asymmetrically substituted pyrazolates offer potential for positional isomerism; however, only a single isomer is observed in each case. Though non-trivial in lieu of crystallographic data, assignment of the specific isomer obtained can be achieved with recourse to spectroscopic data. Thus, for each of **4** and **5** a notable coupling ($J_{FP} \sim 20$ Hz) is apparent between the CF₃ substituent and the phosphacarbon only; this would imply proximity of the two moieties, strongly suggesting that the bulkier CF₃ substituent (*cf.* H or Me) is more favorably positioned away from the sterically encumbered metal center. This is supported by significant deshielding of the phosphacarbon center, consistent with proximity to an electron withdrawing substituent. Indeed, we find the resonant frequency of the phosphacarbon center to be very sensitive to the pyrazolyl substituents (*vide infra*), most significantly so for that at the proximal site.



Scheme 3. Synthesis of [Ru{ η^1 -N: η^2 -P,C-P(pz^{Ph})=CH(SiMe₂R)}(CO)(PPh₃)₂] (R = Me **6a**, C₆H₄CF₃-*p* **6d**) (L = PPh₃). Reagents and conditions: (i) Lipz^{Ph}, THF.

Assignment of the isomeric preference in **6a** and **6d** is a more complex undertaking, given the lack of any direct spectroscopic handle, though the same steric arguments can reasonably be applied. A more electron-withdrawing character is apparent, relative to pyrazole itself (δ_P 64.4 **6a**, *cf.* 58.7 **2a**), which conforms to expectation and is again consistent with the precedent systems, though the modest level of deshielding is inadequate to unequivocally confirm substituent proximity to the phosphacarbon. Nonetheless, we believe this to be the most likely scenario.

2.2. Spectroscopic Features and Trends

The key NMR spectroscopic data for all compounds **2**, **3**, **4** and **5**, along with **6a** and **6d** are summarized in Table 1. As one would anticipate, the pz^{Me2} derivatives impart significant shielding to the phosphacarbon “P” center, which resonates around 25 ppm to lower frequency than for the pz systems; conversely, the presence of an electron-withdrawing CF₃ substituent leads to appreciable deshielding of this site ($\Delta\delta_P \sim +20$), though this is moderated in the pz^{Me,CF3} derivatives by competitive induction from the methyl. All complexes featuring a methyl substituent proximal to the metal also exhibit additional shielding of one PPh₃ ligand ($\Delta\delta_P -3$) compared to their non-alkylated analogues; significantly, the extent of this effect is quantitatively comparable whether the second substituent is methyl or trifluoromethyl, which would imply a localized effect, and also offers further support for the isomeric assignment. The presence of a methyl proximal to the metal also leads to an appreciable decrease in the magnitude of the alkenic C–H coupling constant. This implies reduced *s*-character in this linkage, consistent with an increased contribution from $d_{\pi} \rightarrow \pi^*_{(CP)}$ retrodonation (the result of increased electron density at the metal) and thus greater pyramidalization; indeed, this concurs with structural data for **3d** (*vide supra*).

Influence of the pyrazole upon the alkenic carbon center is also apparent, but exhibits a less defined trend; in contrast, the nature of the silyl substituent clearly holds significance, the SiMe₃ derivatives being notably more deshielded than their SiMe₂Ar analogues, distinctions between the latter being ill defined. This is consistent with ¹³C-NMR studies of vinyl- [49] and aryl-silanes [50], for which enhanced deshielding of the α -carbon follows from increasing methyl substitution at silicon, presumably reflecting the relative “inductive effect”, given the greater electronegativity of carbon relative to silicon. While carbocentric systems show the reverse shielding trend for the β -center, in the case of **2–6** enhanced deshielding of phosphorus is again noted for the SiMe₃ derivatives. Though the

relatively lower electronegativity of phosphorus (*cf.* carbon) might reasonably be invoked in accounting for this disparity, indirect effects via the synergic metal-ligand binding mode (such complexes have not been considered for the carbocentric silanes) cannot be discounted. Indeed, it is noted that analogues of **2** and **3** featuring a *tert*-butyl [29], rather than silyl, substituent exert a significant shielding effect upon the phosphorus center (δ_P 38.8 (pz); 14.2 (pz^{Me2})), yet deshield the α -carbon nucleus (δ_C 81.6 (pz), 79.8 (pz^{Me2})) even more effectively than does SiMe₃, which would appear counter-intuitive on the basis of purely electronegativity arguments. The relative contributions of ligand→metal σ donation, and $d_{\pi} \rightarrow \pi^*_{(CP)}$ retrodonation for each center must thus be considered contributory, though inadequate data are currently available to quantify this.

Table 1. NMR Spectroscopic data for [Ru(η^1 -N: η^2 -P-C-P(pz')=CH(SiMe₂R))Cl(CO)(PPh₃)₂].

Compound		R	P=C	δ_P^1 PPh ₃	δ_C^2 P=C	δ_H^2 P=CH (¹ J _{CH} /Hz) ³
2 ⁴ (pz' = pz)	2a	Me	58.7	46.6, 42.0	45.1	1.59 (137)
	2b	Ph	57.0	47.0, 41.7	42.6	1.72 (135)
3 (pz' = pz ^{Me2})	3a	Me ⁴	32.9	46.6, 39.2	44.9	1.62 (123)
	3b	Ph ⁴	32.3	47.0, 38.9	41.8	1.77 (128)
	3c	C ₆ H ₄ Me- <i>p</i> ⁵	32.6	46.7, 39.1	41.8	1.75 (136)
	3d	C ₆ H ₄ CF ₃ - <i>p</i> ⁵	32.1	46.6, 38.6	39.8	1.66 (135)
4 ⁵ (pz' = pz ^{CF3})	4a	Me	76.6	47.7, 41.5	47.1	1.78 (136)
	4b	Ph	74.9	48.0, 41.3	46.7	1.91 (136)
	4c	C ₆ H ₄ Me- <i>p</i>	75.0	47.9, 41.3	45.4	1.90 (134)
	4d	C ₆ H ₄ CF ₃ - <i>p</i>	73.8	47.8, 40.9	43.8	1.82 (134)
5 ⁵ (pz' = pz ^{Me,CF3})	5a	Me	64.6	46.9, 38.4	45.2	1.76 (129)
	5b	Ph	62.7	47.2, 38.3	41.8	1.97 (131)
	5c	C ₆ H ₄ Me- <i>p</i>	61.6	47.2, 38.4	42.1	1.97 (135)
	5d	C ₆ H ₄ CF ₃ - <i>p</i>	62.0	47.1, 37.8	40.7	1.85 (133)
6 ⁵ (pz' = pz ^{Ph})	6a	Me	64.4	47.4, 41.8	47.5	1.74 (137)
	6d	C ₆ H ₄ CF ₃ - <i>p</i>	60.5	47.7, 41.3	43.7	1.78 (136)

¹ Referenced to 85% H₃PO₄; ² Referenced to SiMe₄; ³ Measured from coupled ¹H-¹³C HSQC spectra; ⁴ Recorded as solutions in CD₂Cl₂; ⁵ Recorded as solutions in CDCl₃.

3. Materials and Methods

3.1. General Methods

All manipulations were performed under anaerobic conditions using standard Schlenk line and glovebox (MBraun, Germany) techniques, working under an atmosphere of dry argon or dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å, for DCM and THF) or potassium mirrors. General reagents were obtained from Sigma-Aldrich (Gillingham, UK) or Fisher Scientific (Loughborough, UK) and purified by appropriate methods before use, precious metal salts were obtained from STREM (Cambridge, UK). [RuHCl(CO)(PPh₃)₃] [51], RMe₂SiCH₂PCl₂ (R = Me, Ph [52], Tol [29], C₆H₄CF₃ [39]), RMe₂SiC=P [29,30,40] and [Ru{P=CH(SiMe₂R)}Cl(CO)(PPh₃)₂] (R = Me [29,30], Ph [29], Tol, C₆H₄CF₃-*p* [40]) were prepared as previously described. Unless otherwise stated, NMR spectra were recorded at 303 K on a Varian VNMRs 400 (¹H 399.50 MHz, ¹³C 100.46 MHz, ¹⁹F 375.87, ³¹P 161.71 MHz, ²⁹Si 79.37 MHz) spectrometer (Varian, Yarnton, UK). All spectra are referenced to external Me₄Si, 85% H₃PO₄ or CFCl₃ as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBC) spectra; phosphaaalkenic proton and silicon shifts were determined indirectly by ¹H-³¹P and ¹H-²⁹Si correlation (HMBC). Elemental analyses were obtained by Mr. S. Boyer of the London Metropolitan University Elemental Analysis Service.

3.2. X-Ray Crystallography

Single crystal X-ray diffraction data were recorded on an Agilent Xcalibur Eos Gemini Ultra diffractometer (Agilent Technologies, Yarnton, UK) with CCD plate detector using Cu-K α (λ = 1.54184) radiation. Structure solution and refinement were performed using SHELXS [53] and SHELXL [53] respectively, running under Olex2 [54].

3.3. Syntheses and Characterisation

[Ru(η^1 -N: η^2 -P,C-P(pz^{Me2})=CH(SiMe₂Tol))(CO)(PPh₃)₂] (**3c**): In a representative procedure, following literature precedent for compounds **3a** and **3b** [29,30], Hpz^{Me2} (12.7 mg, 0.13 mmol) as solution in THF was treated, at ambient temperature, with a single equivalence of ⁿBuLi (0.06 cm³, 2.5 M in hexanes) and the mixture stirred for 5 min. The resulting solution was added directly to a solution of [Ru(P=CH(SiMe₂Tol))Cl(CO)(PPh₃)₂] (**1c**, 67 mg, 0.08 mmol) at ambient temperature and the mixture stirred for 1 h. Volatiles were removed under reduced pressure, then the residue extracted with CH₂Cl₂ and the resulting solution filtered; the solvent was removed under reduced pressure and the resulting solid dried in vacuo, before being redissolved in CDCl₃ for spectroscopic analysis. ¹H NMR (CDCl₃): δ_H 0.06 (s, 3H, SiMe₂), 0.15 (s, 3H, SiMe₂), 0.42 (s, 3H, Pz*-Me), 1.75 (m, 1H, CHSi (¹J_{C-H} = 135.31 Hz)), 1.95 (s, 3H, Pz*-Me), 2.34 (s, 3H, CH₃), 5.04 (s, 1H, Pz*-H4), 7.08–7.42 (m, 35H, Ar-H). ¹³C{¹H} NMR (CDCl₃): δ_C -0.9 (d, ³J_{C-P} = 7.6 Hz, SiCH₃), 0.16 (d, ³J_{C-P} = 8.5 Hz, SiCH₃), 9.6 (d, ³J_{C-P} = 5.3 Hz, Pz-CH₃), 11.9 (s, Pz-CH₃), 21.6 (s, CH₃), 41.8 (ddd, J_{C-P} = 4.5, 31.3, 78.6 Hz, CHSi (¹J_{C-H} = 136.3 Hz)), 105.0 (d, J_{C-P} = 2.7 Hz, Pz*-C4), 127.6 (d, J_{C-P} = 8.87 Hz, Ar-C), 127.8 (d, J_{C-P} = 8.87 Hz, ArC), 128.2 (s, ArC), 128.6 (m, ArC), 128.9 (d, J_{C-P} = 6.7 Hz, ArC), 130.4 (d, J_{C-P} = 13.0 Hz, ArC), 133.8 (m, ArC), 133.6–134.4 (m, ArC), 137.4 (s, ArC), 138.2 (d, J_{C-P} = 30.7 Hz, ArC), 138.4 (d, J_{C-P} = 31.8 Hz, ArC), 145.2 (s, Pz*-C5), 152.4 (s, Pz*-C3), 209.5 (br, CO). ³¹P{¹H} NMR (CDCl₃): δ_P 46.7 (d, J_{P-P} = 16.9 Hz), 39.1 (dd, J_{P-P} = 50.1, 16.7 Hz), 32.6 (d, J_{P-P} = 50.4 Hz, P=C). ²⁹Si{¹H} NMR (CDCl₃): δ_{Si} -5.3.

[Ru(η^1 -N: η^2 -P,C-P(pz^{Me2})=CH(SiMe₂C₆H₄CF₃-p))(CO)(PPh₃)₂] (**3d**): In comparable fashion to **3c**, from the respective phosphaaalkenyl (**1d**). ¹H NMR (CDCl₃): δ_H -0.02 (s, 3H, SiCH₃), 0.18 (s, 3H, SiCH₃), 0.42 (s, 3H, Pz*-Me), 1.66 (m, 1H, CHSi (¹J_{C-H} = 135.3 Hz)), 1.95 (s, 3H, Pz*-Me), 5.07 (s, 1H, Pz*-H4), 7.09–7.34 (m, 35H, Ar-H), 7.45–7.56 (m, 4H, C₆H₄CF₃). ¹⁹F NMR (CDCl₃): δ_F -63.06 (s). ¹³C{¹H} NMR (CDCl₃): δ_C -1.3 (d, ³J_{C-P} = 8 Hz, SiCH₃), 0.3 (d, ³J_{C-P} = 8 Hz, SiCH₃), 9.6 (d, ³J_{C-P} = 5.3 Hz, Pz-CH₃), 11.9 (s, Pz-CH₃), 39.8 (br, (¹J_{C-H} = 135.3 Hz) CHSi), 105.2 (d, J_{C-P} = 2.9 Hz, Pz*-C4), 123.8 (q, ²J_{C-F} = 3.9 Hz, CCF₃), 130.9 (q, ¹J_{C-F} = 240.0 Hz, CF₃), 127.6–129.1, 134.1–135.5, 137.2–138.1 (3 \times m, PPh₃, C₆H₄), 145.3 (d, ²J_{C-P} = 1.5 Hz, Pz*-C5), 152.7 (s, Pz*-C3), 209.7 (br, CO). ³¹P{¹H} NMR (CDCl₃): δ_P 46.6 (d, ²J_{P-P} = 16.2 Hz, PPh₃), 38.6 (dd, ²J_{P-P} = 54.4, 16.2 Hz, PPh₃), 32.1 (d, ²J_{P-P} = 51.4 Hz, P=C). ²⁹Si{¹H} NMR (CDCl₃): δ_{Si} -4.5. ν_{CO} = 1913 cm⁻¹. Anal. Found: C, 62.90; H, 5.01; N, 2.90; Calcd for C₅₂H₄₈F₃N₂OP₃RuSi: C, 62.71; H, 4.86; N, 2.81. Crystal data for **3d**: C₅₃H₄₈F₃N₂OP₃RuSi·CHCl₃, M_w = 1115.42, triclinic, *P*-1 (No. 2), *a* = 10.5494(5), *b* = 11.5375(6), *c* = 21.871(1) Å, α = 76.877(4), β = 82.084(4), γ = 85.941(4), *V* = 2565.46(2) Å³, *Z* = 2, *D_c* = 1.444 Mg m⁻³, μ (Cu-K α) = 5.439 mm⁻¹, *T* = 173(2) K, 9464 independent reflections, full-matrix *F*² refinement *R*₁ = 0.0567, *wR*₂ = 0.1894 on 8126 independent absorption corrected reflections [*I* > 2 σ (*I*); 2 θ_{max} = 143.4°], 607 parameters. The empirical absorption correction was conducted using spherical harmonics, as implemented in the SCALE3 ABSPACK scaling algorithm (CryAlisPro Version 1.171.38.41). CCDC 1502285.

[Ru(η^1 -N: η^2 -P,C-P(pz^{CF3})=CH(SiMe₂Tol))(CO)(PPh₃)₂] (**4c**): In comparable fashion to **3**, but commencing from Hpz^{CF3}. ¹H NMR (CDCl₃) δ_H -0.1 (s, 3H, SiCH₃), 0.1 (s, 3H, SiCH₃), 1.90 (m, 1H, CHSi), 2.35 (br, 3H, CH₃), 5.30 (s, 1H, Pz-H3), 5.57 (1 H, s, Pz-H4), 7.04–7.48 (m, 35H, C₆H₅). ¹⁹F NMR (CDCl₃) δ_F -60.4 (d (⁴J_{F-P} = 17.6 Hz)). ¹³C{¹H} NMR (CDCl₃) δ_C -0.9 (d, ³J_{C-P} = 10 Hz, SiCH₃), -0.25 (d, ³J_{C-P} = 5 Hz, SiCH₃), 21.9 (s, CH₃), 45.4 (ddd, J_{C-P} = 80.5, 31.0, 4.8 Hz, (¹J_{C-H} = 134 Hz), SiCH), 105.2 (s, Pz-C⁴), 119.1 (q, ¹J_{C-F} = 269 Hz, CF₃), 128.2–128.6, 128.7–129.2, 133.7–134.4, 137.6–138.0 (4 \times m, CH), 140.9 (s, Pz-C3), 210.5 (t, ²J_{C-P} = 13 Hz, C \equiv O). ³¹P{¹H} NMR (CDCl₃) δ_P 75.0 (dq, ²J_{P-P} = 44.5 Hz,

$^4J_{P-F} = 17.50$ Hz, $P=CH$), 47.9 (d, $^2J_{P-P} = 17.5$ Hz, PPh_3), 41.3 (dd, $^2J_{P-P} = 44.5$, 17.5 Hz, PPh_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ −5.6. Anal. Found: C, 62.10; H, 4.85; N, 2.91; Calcd for $C_{51}H_{46}F_3N_2OP_3RuSi$: C, 62.39; H, 4.72; N, 2.85.

[$Ru\{\eta^1-N:\eta^2-P,C-P(pz^{CF_3})=CH(SiMe_2C_6H_4CF_3-p)\}(CO)(PPh_3)_2$] (**4d**): As for **4c**, commencing from **1d**. 1H NMR ($CDCl_3$) δ −0.06 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 1.85 (m, 1H, $CHSi$), 5.32 (s, 1H, $Pz-H3$), 5.60 (s, 1H, $Pz-H4$), 7.05–7.39 (m, 30H, C_6H_5), 7.5 (d, 2H, $J_{H-F} = 8.0$ Hz, C_6H_4), 7.63 (d, 2H, $J_{H-F} = 7.6$ Hz, C_6H_4). ^{19}F NMR ($CDCl_3$) δ −60.1 (d ($^4J_{F-P} = 19.4$ Hz)), −62.7 (s, $C_6H_4CF_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.2 (s, $SiCH_3$), 43.8 (br. ($^1J_{C-H} = 134$ Hz), $SiCH$), 104.9 (s, $Pz-C4$), 128.0 (t, $J_{C-P} = 4.3$ Hz, CH), 128.7 (d, $J_{C-P} = 7.3$ Hz, CH), 128.9 (s, CH), 129.5 (s, CH), 132.2–132.6, 133.5–134.1 ($2 \times$ m, CH), 142.8 (s, $Pz-C5$), 145.4 (br. $Pz-C3$). CF_3 resonances obscured by aromatics. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.8 (dd, $^2J_{P-P} = 47.4$, 15.8 Hz), 47.1 (d, $^2J_{P-P} = 15.8$ Hz, PPh_3), 62.0 (dq, $^2J_{P-P} = 47.4$ Hz, $^4J_{P-F} = 19.40$ Hz, $P=CH$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ −4.2. $\nu_{CO} = 1913$ cm^{-1} .

[$Ru\{\eta^1-N:\eta^2-P,C-P(pz^{Me,CF_3})=CH(SiMe_2Tol)\}(CO)(PPh_3)_2$] (**5c**): As for **4c**, but commencing from Hpz^{Me,CF_3} . 1H NMR ($CDCl_3$): δ_H −0.03 (s, 3H, $SiCH_3$), 0.17 (s, 3H, $SiCH_3$), 0.55 (s, 3H, $Pz-CH_3$), 1.97 (br, 1H, $CHSi$), 2.36 (s, 3H, CH_3), 5.52 (br. $Pz-H4$), 7.12–7.50 (m, 34 H, $2 \times PPh_3$, C_6H_4). ^{19}F NMR ($CDCl_3$): δ_F −59.9 (d, $J_{F-P} = 19.4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C −1.1 (d, $^3J_{C-P} = 7.8$ Hz, $SiCH_3$), 0.14 (d, $^3J_{C-P} = 8.8$ Hz, $SiCH_3$), 11.85 (s, $Pz-CH_3$), 21.6 (m, CH_3), 42.1 (br. ddd, $J_{C-P} = 28.2$, 78.8 Hz, $^1J_{C-H} = 137$ Hz, $SiCH$), 105.7 (br m, $Pz-C4$), 119.5 (br, $^1J_{C-F} = 269$ Hz, CF_3), 127.6–130.3 (m, PPh_3), 133.5–135.1 (m, PPh_3 , C_6H_4), 137.6 (dd, $J = 1.49$, 30.1 Hz, $Pz-C5$), 152.6 (br, $Pz-C3$), 209.0 (m, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 61.62 (dq, $^2J_{P-P} = 45.7$, $^4J_{P-F} = 19.3$ Hz, $P=C$), 47.2 (d, $^2J_{P-P} = 16.4$ Hz, PPh_3), 38.4 (ddd, $^2J_{P-P} = 45.7$, 16.4, $J_{P-F} = 1.4$ Hz, PPh_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ_{Si} −5.7. $\nu_{CO} = 1918$ cm^{-1} . Anal. Found: C, 62.42; H, 5.05; N, 2.89; Calcd for $C_{52}H_{48}F_3N_2OP_3RuSi$: C, 62.71; H, 4.86; N, 2.81.

[$Ru\{\eta^1-N:\eta^2-P,C-P(pz^{Me,CF_3})=CH(SiMe_2C_6H_4CF_3-p)\}(CO)(PPh_3)_2$] (**5d**): As for **5c**, but commencing from **1d**. 1H NMR ($CDCl_3$): δ_H 0.01 (s, 3H, $SiCH_3$), 0.21 (s, 3H, $SiCH_3$), 0.56 (s, 3H, $Pz-CH_3$), 1.85 (br, 1H, $CHSi$), 5.54 (s, 1H, $Pz-H4$), 7.13–7.28, 7.37–7.46, 7.47–7.53, 7.58–7.67 ($4 \times$ m, 34H, PPh_3 , C_6H_4). ^{19}F NMR ($CDCl_3$): δ_F −59.9 (d, $J = 20.3$ Hz, $Pz-CF_3$), −62.7 (s, CF_3-p). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C −1.4 (d, $^3J_{C-P} = 7.4$ Hz, $SiCH_3$), 0.16 (d, $^3J_{C-P} = 8.0$ Hz, $SiCH_3$), 11.9 (s, $Pz-CH_3$), 40.7 (ddd, $J_{C-P} = 32.9$, 79.8, 5.0 Hz, $^1J_{C-H} = 137$ Hz, $SiCH$), 105.9 (br m, $Pz-C4$), 119.4 (q, $^1J_{C-F} = 270$ Hz, CF_3), 124.6 (q, $^1J_{C-F} = 272$ Hz, CF_3), 127.6–128.0 (m, CH), 128.6 (d, $J = 7$ Hz, CH), 128.5–129.1 (m, CH), 133.6–134.3 (m, CH), 137.6 (dd, $J = 1.3$, 3.2 Hz, $Pz-C5$), 152.8 (br, $Pz-C3$), 209.1 (m, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 61.99 (dq, $^2J_{P-P} = 57.0$, $^4J_{P-F} = 18.8$ Hz, PPh_3), 47.1 (d, $^2J_{P-P} = 15.8$ Hz, PPh_3), 37.8 (dd, $^2J_{P-P} = 47.0$, 15.9, $P=C$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ_{Si} −4.16. $\nu_{CO} = 1917$ cm^{-1} .

[$Ru\{\eta^1-N:\eta^2-P,C-P(pz^{Ph})=CH(SiMe_3)\}(CO)(PPh_3)_2$] (**6a**): In a comparable fashion, commencing from **1a** and Hpz^{Ph} . 1H NMR ($CDCl_3$): δ_H 0.15 (s, 9H, $Si(CH_3)_3$), 1.74 (m, 1H, $CHSi$), 5.39 (s, 1H, $Pz-H3$), 5.56 (br. $Pz-H4$), 7.05–7.55 (m, 35H, PPh_3 , C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C 1.4 (d, $^3J_{C-P} = 5.5$ Hz, $Si(CH_3)_3$), 47.5 (ddd, $^2J_{P-P} = 4.4$, 31.0, 80.2 Hz, $^1J_{C-H} = 135.9$ Hz, $SiCH$), 103.3 (d, $J_{C-P} = 3.2$ Hz, $Pz-C4$), 127.4 (d, $J_{C-P} = 6.6$ Hz, CH), 127.7 (d, $J_{C-P} = 8.7$ Hz, CH), 128.1 (d, $J_{C-P} = 8.6$ Hz, CH), 128.6 (s, CH), 128.8 (d, $J_{C-P} = 19.0$ Hz, CH), 129.1 (s, CH), 133.9 (m, CH), 137.3 (d, $J_{C-P} = 9.7$ Hz, *ipso*-C), 137.7 (d, $J_{C-P} = 32.0$ Hz, *ipso*-C), 138.0 (d, $J_{C-P} = 32.0$ Hz, *ipso*-CH), 141.0 (s, $Pz-C3$), 147.7 (br, $Pz-C5$), 210.7 (m, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 64.4 (d, $J_{P-P} = 46.2$ Hz, $P=C$), 47.4 (d, $J_{P-P} = 18.5$ Hz, PPh_3), 41.8 (dd, $J_{P-P} = 46.2$, 18.4 Hz, PPh_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ_{Si} −0.5. $\nu_{CO} = 1908$ cm^{-1} . Anal. Found: C, 65.71; H, 5.18; N, 3.03; Calcd for $C_{46}H_{47}N_2OP_3RuSi$: C, 65.62; H, 5.33; N, 2.99.

[$Ru\{\eta^1-N:\eta^2-P,C-P(pz^{Ph})=CH(SiMe_2C_6H_4CF_3-p)\}(CO)(PPh_3)_2$] (**6d**): As for **6a**, but commencing from **1d**. 1H NMR ($CDCl_3$): δ_H −0.03 (s, 3H, $SiCH_3$), 0.27 (s, 3H, $SiCH_3$), 1.86 (m, 1H, $CHSi$), 5.56 (1H, s, $Pz-H4$), 5.60 (s, 1H, $Pz-H5$), 7.11–7.68 (m, 39 H, $2 \times PPh_3$, C_6H_5 , C_6H_4). ^{19}F NMR ($CDCl_3$): δ_F 62.62 (s, CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C −1.3 (d, $^3J_{C-P} = 8$ Hz, $SiCH_3$), −0.9 (d, $^3J_{C-P} = 5$ Hz, $SiCH_3$), 45.6 (ddd, $J_{C-P} = 5.1$, 31.4, 79.5 Hz, $^1J_{C-H} = 133.9$ Hz, $SiCH$), 103.5 (d, $J_{C-P} = 3.3$ Hz, $Pz-C4$), 124.5 (q, $^1J_{C-F} = 272$ Hz, CF_3), 127.4–130.2, 133.7–134.5 ($2 \times$ m, PPh_3 , C_6H_5 , C_6H_4), 141.2 (s, $Pz-C3$), 147.9 (br. $Pz-C5$), 210.5 (m, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 60.6 (d, $^2J_{P-P} = 46.9$ Hz, $P=C$), 47.7 (d, $^2J_{P-P} = 17.4$ Hz, PPh_3), 41.3 (dd, $^2J_{P-P} = 46.9$, 17.4 Hz, PPh_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ_{Si} −4.9. $\nu_{CO} = 1912$. Anal. Found: C, 64.02; H, 4.69; N, 2.71; Calcd for $C_{53}H_{48}F_3N_2OP_3RuSi$: C, 64.11; H, 4.77; N, 2.80.

4. Conclusions

We have described the synthesis of an extended range of pyrazolyl-bridged η^2 -phosphaalkene complexes of ruthenium(0), obtained by the reaction of pyrazolates with ruthenaphosphaalkenyl complexes. Spectroscopic and structural data suggest the nature of the pyrazolyl substituents in the 3/5 positions has a significant influence on the nature of the phosphaalkene fragment, which is a balance of direct shielding/deshielding of the phosphorus center, and an indirect influence resulting from donation to the metal, mediated through the extent of metal-ligand retro-donation. In contrast, the nature of the silyl substituents exerts a much smaller, albeit still noticeable, influence. Presently, the available data pool is inadequate to formulate an unequivocally quantitative description of these effects, which are the subject of on-going investigations.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2304-6740/4/4/30/s1>, crystal data for compound **3d** in cif format (CCDC 1502285); supplementary file containing illustrative ^{13}C and ^{31}P NMR spectra for compounds **3c** (Figures S1 and S2), **4c** (Figures S3 and S4), **5d** (Figures S5 and S6), **6a** (Figures S7 and S8).

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Conflicts of Interest: The authors declare no conflict of interest.

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